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Contributions of Natural Emissions to Ozone and $PM_{2.5}$ as Simulated by the Community Multiscale Air Quality (CMAQ) Model

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Supporting Information

ABSTRACT: The relative roles of natural and anthropogenic sources in determining ozone and fine particle concentrations over the continental United States (U.S.) are investigated using an expanded emissions inventory of natural sources and an updated version of the Community Multiscale Air Quality (CMAQ) model. Various 12-month CMAQ simulations for the year 2002 using different sets of input emissions data are combined to delineate the contributions of background pollutants (i.e., model boundary conditions), natural emissions, anthropogenic emissions, as well as the specific impacts of lightning and wildfires. Results are compared with observations and previous air quality model simulations. Wildfires and lightning are both identified as contributing significantly to ozone levels with lightning NO_x adding as much as 25−30 ppbV (or up to about 50%) to surface 8-h average natural O_3 mixing ratios in the southeastern U.S. Simulated wildfire emissions added more than 50 ppbV (in some cases >90%) to 8-h natural O_3 at several locations in the west. Modeling also indicates that natural emissions (including biogenic, oceanic, geogenic and fires) contributed ≤40% to the annual average of total simulated fine particle mass over the eastern two-thirds of the U.S. and >40% across most of the western U.S. Biogenic emissions are the dominant source of particulate mass over the entire U.S. and wildfire emissions are secondary. Averaged over the entire modeling domain, background and natural ozone are dominant with anthropogenically derived ozone contributing up to a third of the total only during summer. Background contributions to fine particle levels are relatively insignificant in comparison. Model results are also contrasted with the U.S. Environmental Protection Agency (EPA) default values for natural light scattering particle concentrations to be used for regional haze regulatory decision-making. Regional differences in EPA guidance are not supported by the modeling and EPA uncertainty estimates for default values are far smaller than the modeled variability in natural particle concentrations.

INTRODUCTION

Air pollution regulations focus on mitigating anthropogenic influences to protect human health and ecosystems. However, natural pollutants will always represent a limit to how low certain air pollutant levels can be reasonably reduced. Natural pollutants are those derived from natural processes only, free from anthropogenic influences. However, "background" pollutants are usually considered those that are free of local influences with "local" defined arbitrarily. For our purposes, background over the United States (U.S.) represents pollutant concentrations that are not influenced by anthropogenic emissions from the U.S. and adjacent regions in Canada and Mexico. Estimates of natural and background pollutant levels are typically made in one of two ways. An empirical approach uses observations, contaminated by human influence, and a combination of statistical methods and heuristic arguments to estimate "natural" levels. The other approach uses modeling and various methods for tracking or otherwise extracting source contributions to isolate natural influences. Both methods involve assumptions that introduce uncertainties.

Several efforts to estimate background and natural pollutant levels have been made within the past decade. This work (see Supporting Information) has produced estimates of background plus natural (B + N) ozone in the range of 20−50 ppbV, depending on location and season.[1−3] In 2003 the U.S. Environmental Protection Agency (EPA) published a list of natural aerosol concentrations that it believes are typical of pristine areas.[4] Several studies have been published that use global models to derive B + N particle concentrations over the U.S.[5−7] These suggest that U.S. B + N levels are ∼1 $\mu g\ m^{-3}$ for organic carbon (OC) aerosol mass, <0.1 $\mu g\ m^{-3}$ for elemental carbon (EC) aerosol mass, ∼0.4 $\mu g\ m^{-3}$ for ammonium sulfate, and between 0.25 and 0.40 $\mu g\ m^{-3}$ for ammonium nitrate.

In general, natural ozone and nitrate aerosol levels are primarily associated with NO_x emissions from soil, lightning and biomass burning along with wildfire and biogenic volatile organic carbon (VOC) emissions. Natural sulfur emissions come from the oceans, lakes, wetlands, geogenic sources (volcanoes, hot springs and fumaroles), and biomass burning. Ammonia is emitted naturally by oceans, biomass burning, crops, soils and wild animals. Previous papers [8,9] describe a revised set of natural

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emissions for use in the EPA Community Multiscale Air Quality (CMAQ) model and changes in CMAQ to enable more complete simulations of natural pollutants. Simulations by this revised model included emissions from natural sources previously listed but neglected crops and fertilized soils. The current paper describes the simulated spatial and temporal variability of naturally occurring U.S. pollutants such as ozone and fine particles (i.e., particles with a mean diameter <2.5 μm, $PM_{2.5}$).

MODELING APPROACH

Modeling of 2002 builds on previous work and enables comparisons with the regulatory analyses done by the VISTAS (Visibility Improvement State and Tribal Association of the Southeast) Regional Planning Organization (RPO). VISTAS, composed of air regulatory and land management representatives from 10 Southeast states (http://vistas-sesarm.org/), is one of five RPOs charged with developing strategies for implementing the Regional Haze Rule. VISTAS simulated 2002 air quality using CMAQ version 4.4 (CMAQ4.4) and version 4.5 (CMAQ4.5). These efforts produced several evaluated modeling products. Our modeling methodology—described in the Supporting Information along with a comparison between results from the current effort and the VISTAS effort—used a version of CMAQ referred to hereafter as "CMAQ4.6*".

CMAQ version 4.6 required revisions to enable it to process an enhanced data set of chlorine, organic sulfur and H_2S natural emissions[8] and to more realistically treat secondary organic aerosol (SOA) formation. The revised version (CMAQ4.6*) uses the CB05 chemical mechanism with reactions added to treat various chlorine and sulfur compounds not otherwise simulated.[9] Changes to CB05 included reactions added to both the gas-phase and heterogeneous chemistry along with other cloud chemistry module revisions that update the treatment of the gas-aqueous interface. Also, CMAQ4.6 does not adequately treat the semivolatile nature of primary aerosols and has limited treatment of SOA formation.[10] In CMAQ4.6* we implemented the SOA improvements described by Morris et al. [10] but did not address primary semivolatile OC. Thus, CMAQ likely underestimates primary (and possibly total) OC mass when thermodynamics favor semivolatile aerosol formation.

Model boundary conditions (BCs) play an important role in determining pollutant levels across the modeling domain. We defined BCs following the VISTAS approach, using 3-h values in multiple layers from a GEOS-Chem global 2002 simulation.[11] Variations in boundary-averaged BCs are illustrated in the Supporting Information.

Model results based on all emissions (using a 36 × 36 km cell grid) compared well for ozone. Overall bias in daily maximum 8-h ozone was <3 ppbV and mean fractional bias (MFB) was only 6%. CMAQ4.6* underestimated sulfate across the domain (MFB=-23%) but these values were greater than those from VISTAS across the eastern U.S. (Supporting Information Table S-7). Finally, OC mass was biased low across the eastern and high across the western U.S. (Supporting Information Table S-3).

RESULTS AND DISCUSSION

Several 12-month emission scenarios were modeled for the purpose of identifying specific air quality influences from different source categories. The "all natural" scenario is one that omitted anthropogenic emissions while the "total emissions" scenario refers to one that combined the man-made emissions modeled by VISTAS for its regional haze analyses[12] with the all natural emissions scenario. Additional scenarios were run using natural emissions minus lightning or wildfires. Results from different simulations were subtracted to infer contributions associated with different emission categories.

Background. Background levels are determined by model BCs of primary pollutants and precursors. Boundaries of the CMAQ model grid were located >450 km away from the continental U.S. except along the eastern edge where the boundary passed within 250 km of eastern Maine. Highest average BCs for particulate sulfate, ammonium, OC and EC were along the southern boundary while the lowest occurred along the northern boundary (Supporting Information).

BC effects were greatest along the domain edges and decreased inward. Background O_3 accounted for 47−93% on average across the modeling domain. The highest relative background contributions occurred in winter and early spring while the lowest contributions occurred in summer when on-grid emissions play a larger role. The grid-averaged background contributions to particles were much smaller than for ozone, averaging 1−11% for sulfate, 0−18% for OC, and 1−13% for $PM_{2.5}$. Background contributions to OC and $PM_{2.5}$ were greatest in April and May (see Supporting Information)

Natural Emissions. Outputs from the CMAQ4.6* simulations are summarized using results representing 50 receptors or locations as described in the Supp. Inf. These are sorted into two groups representing West and East U.S. regions similar to that done by the EPA.[4] The spatial and temporal variability of natural ozone and particulate matter near the ground may eventually become critical in developing emissions management options for achieving compliance with air pollutant standards. Ozone was examined using the daily maximum 8-h average mixing ratio (ξ^*_{8hO3}), the primary regulatory O_3 metric in the U.S. $PM_{2.5}$ mass and its components were examined using the 24-h (C_{24hPM}) and annual (C_{YrPM}) average concentrations, both of these also being regulatory metrics. East−west regional differences in speciated C_{24hPM} were examined for comparison with the EPA default values for light-obscuring particulate matter.

Ozone. The transitory nature of wildfires and lightning compared with anthropogenic NO_x sources suggests that ozone peaks caused by natural sources will tend to be brief but high. Peak one hour O_3 mixing ratios from the all natural scenario met that expectation (Supporting Information, Table S-3). Across the continental U.S. the B + N ozone peaks tended to be highest in the West (near fires) and lowest in the extreme northwest and upper Midwest. Fire emissions were a major factor contributing to all B+N levels exceeding 100 ppbV.

Maximum simulated B + N ξ^*_{8hO3} values for 2002 occurred across the western U.S. and eastern Canada (Figure 1). For the 50-receptor subset, the largest B + N ξ^*_{8hO3} value—138 ppbV—was simulated in northern California (site RDP). In the east, the highest simulated B+N ξ^*_{8hO3} values were 66 ppbV in New York City (NYC) and 62 ppbV in Detroit (DET). Across all western sites, the *average* annual maximum B + N ξ^*_{8hO3} was 70 ppbV, while the equivalent value in the East was 54 ppbV. The U.S. ozone air quality regulatory standard, currently 75 ppbV [computed as the annual fourth highest ξ^*_{8hO3} (i.e., 98th percentile for an April−October ozone monitoring season) averaged over three years], is not much greater than the values computed in the East and is far below the highest values in the West. The site variability of B + N ξ^*_{8hO3} is illustrated in Figure 2.

Seven western sites and all eastern sites had 98th percentile ξ^*_{8hO3} >60 ppbV.

$PM_{2.5}$ Mass and Components. Simulated B + N C_{24hPM} values were generally greater at West receptors. The mean eastern B + N C_{24hPM} was 2.5 $\mu g\ m^{-3}$ while in the West it was 4.7 $\mu g\ m^{-3}$. Seasonal variations in natural C_{24hPM} depend on the seasonality of emissions. Wildfires are especially important because they contribute more to $PM_{2.5}$ than other natural sources. Fires also give West receptors greater variability in B + N C_{24hPM} (Supporting Information, Figure S-5). The fifth-95th percentile interval of B+N C_{24hPM} for East receptors was 0.4−7.0 $\mu g\ m^{-3}$ and for the West was 0.3−18 $\mu g\ m^{-3}$.

EPA haze guidance [4] is for evaluating progress toward the "natural background" objective in places where visibility is an intrinsic value to be protected. The EPA suggests default particle concentrations (C_{def}) for estimating 24-h *natural* light scattering (β^*_{scat}). These defaults are the baseline against which simulated B + N values should be compared. The haze regulation requires reductions in total light scattering (β_{scat}) to levels ≤ β^*_{scat} on the "worst 20 percent" of all days in a year. Here we compare C_{def} values with simulated B + N values (C_{sim}) for the worst 20% of all days in 2002 with the days selected based on total (including anthropogenic) $PM_{2.5}$ mass rather than β_{scat}. Additional comparisons between C_{def} and C_{sim} are summarized in Supporting Information.

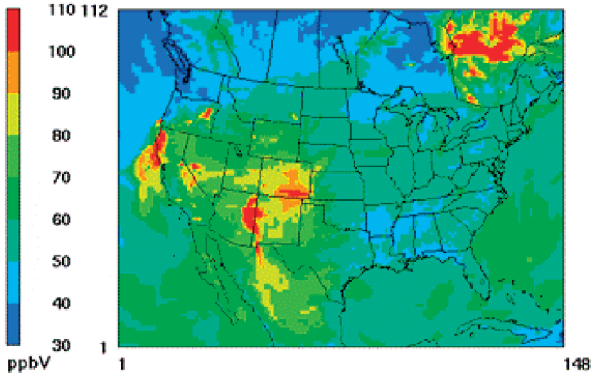

Figure 1. Simulated daily maximum 8-h average surface O_3 mixing ratio in each grid cell of the modeling domain for 2002 based on natural emissions only.

Figure 3 compares regionally averaged C_{sim} and C_{def} and their associated uncertainties. Uncertainty in C_{sim} (represented in Figure 3 by the 90% confidence intervals (CIs) of the regionally averaged "worst 20 percent" set of days) is large compared to differences between C_{sim} and C_{def} and compared to the EPA-expressed uncertainty in C_{def}. Of the 12 species + region pairings in Figure 3, the mean C_{sim} value is within the EPA uncertainty of C_{def} for only four cases: NH_4NO_3 and dust in the West; NH_4 + SO_4 and OC in the East. In the West, simulated sulfate aerosol mass [i.e., the sum of particulate sulfate and associated ammonium, $NH_4 + SO_4$, in a form that is usually not fully neutralized as $(NH_4)_2SO_4$] is larger than C_{def} but in the East C_{sim} and C_{def} are similar. Also, the $NH_4 + SO_4$ C_{sim} average in the West is greatly skewed by high concentrations causing the average to fall near the top of the 90-percent CI for western $NH_4 + SO_4$ C_{sim}. This result is due primarily to wildfires. Dimethylsulfide (DMS) and H_2S emissions along the Gulf of Mexico coast predominantly influence coastal sulfate concentrations.[9] Greater precipitation in the East results in more atmospheric scavenging of aerosols and precursor gases. Thus, the West-East differences in C_{def} are likely not realistic unless non-U.S. anthropogenic emissions are included with natural emissions. Regardless, the large variability in NH_4+SO_4 concentrations makes using regional averages problematic for regulatory applications.

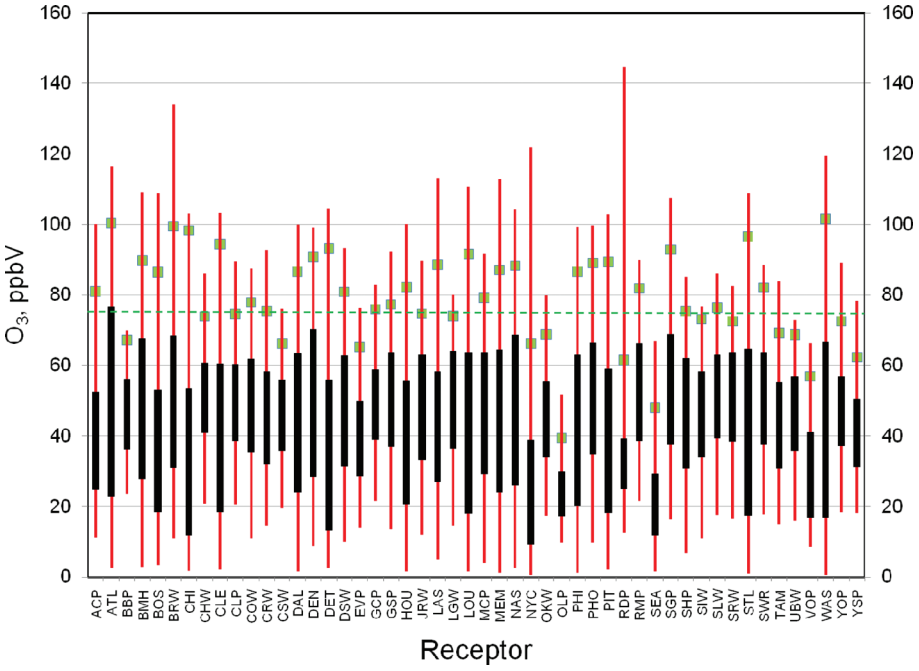

Figure 2. Variation in daily maximum 8-h O_3 mixing ratios (ξ^*_{8hO3}) for 2002 simulated at 50 receptors from natural emissions only and including background (model boundary) influences. Red lines denote the total range in daily values, the black bars denote the range between the 20th and 80th percentile values, and the green squares denote the 98th percentile values. Site locations are shown in Supporting Information, Figure S-3. The 8-h O_3 air quality standard of 75 ppbV is shown by the dashed line.

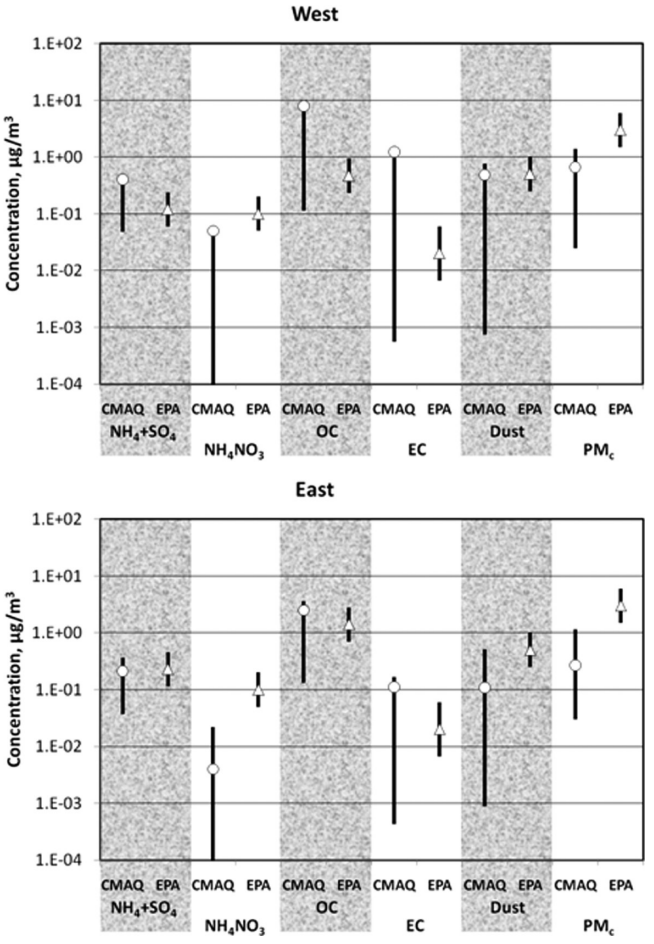

Figure 3. Comparison of EPA default values (triangles) for natural light scattering particles and simulated B+N values for the "worst 20 percent days" (see text for details). Vertical lines represent uncertainty in the EPA defaults and the 90% confidence intervals for simulated values. Circles denote simulated regional average values. The lower end of the simulated NH_4NO_3 confidence interval is actually near 1×10^{-5} $\mu g\ m^{-3}$ for both regions.

The OC C_{sim} average for the West is greater (by a factor of 3) than in the East whereas C_{def} is nearly a factor of 3 greater in the East, but this disagreement between C_{sim} and C_{def} is on a weaker footing than it is for sulfate. Natural OC in the West comes mostly from fires whereas in the East it originates primarily as a secondary aerosol byproduct of VOC oxidation. Biases in CMAQ OC levels (Supporting Information) could mean that modeled East−west differences are not as large as implied by these results. Natural EC is emitted solely by fires and unlike OC is not likely affected by model chemistry bias. EC C_{sim} is higher than C_{def} in both regions but is 10× higher in the West. There is evidence that wildfires (or some combination of sources) may contribute to a high OC C_{sim} bias in the West (see Supporting Information)

Regulatory limits on 24-h (98th percentile) and annual average $PM_{2.5}$ are 35 $\mu g\ m^{-3}$ and 15 $\mu g\ m^{-3}$, respectively. Regulatory standards are based on 3-year averages but examining model results for one year provides insight into the potential that natural emissions might contribute to regulatory compliance problems. Simulated maximum C_{24hrPM} is <10 $\mu g\ m^{-3}$ over half the model grid cells, mostly over the oceans. About one-fifth of grid cells had maximum $C_{24hrPM} \geq 35\ \mu g\ m^{-3}$. As with ozone, the biggest contributor to high $PM_{2.5}$ is wildfires. Figure 4 illustrates the behavior of simulated B + N C_{24hrPM} at each receptor. The overall range in B + N C_{24hrPM} exceeds several orders of magnitude. Two sites (RDP and YSP) had B+N C_{24hrPM} >35 $\mu g\ m^{-3}$ and those sites were affected by fires. Nineteen of the remaining sites had 98th percentile values between 10 and 35 $\mu g\ m^{-3}$. The lowest 98th percentile B + N C_{24hrPM} was 5.5 $\mu g\ m^{-3}$ and the median value excluding RDP and YSP was 9.0 $\mu g\ m^{-3}$ (~25% of the standard). As described in the Supporting Information, natural contributions to annual average $PM_{2.5}$ concentrations are also likely to pose barriers to attaining fine particle standards in some locations.

Contributions from Lightning. The lightning contribution to O_3 in the absence of anthropogenic emissions is occasionally substantial, although the effects of LNO_x may diminish in the presence of anthropogenic NO_x. Also, the influence of LNO_x on O_3 could be enhanced or diminished in the presence of significant anthropogenic VOC emissions. The primary simulated influence of LNO_x was to increase ozone (ξ^*_{8hO3}), especially across the southern U.S. (Supporting Information) When ξ^*_{8hO3} > 40 ppbV modeling indicated increases from LNO_x as high as 10−30 ppbV although we recognize that the magnitude of this response is probably sensitive to model grid cell size (the 36-km cells used here are larger than the 4−5 km cells typically used for ozone modeling). Isolated ξ^*_{8hO3} reductions from LNO_x titration of O_3 were less than 4 ppbV. LNO_x also contributes slightly to OC formation (up to 2% annually in Florida) but very little to other aerosol species (Supporting Information, Table S-6).

Contributions from Wildfires. Wildfire NO_x and VOC emissions are expected to increase ozone (although some local NO titration of ozone is likely near emission "hot spots") and fire particle emissions contribute to $PM_{2.5}$. The 2002 peak in North American wildfire emissions was in July and August. A simulation that excluded wildfires, when compared with results from the natural-only emissions simulation, demonstrated that wildfires contributed as much as 30−50 ppbV to ξ^*_{8hO3} when this metric exceeded 40 ppbV (Supporting Information, Figure S-7). As with LNO_x, occasional O_3 titration was also simulated. Modeled wildfires contributed more than 10% to C_{YrPM} in 5 of 8 U.S. regions with the highest contribution (30%) occurring in California (Supporting Information, Table S-6). Fire emissions also contributed 7−10% of the B + N $PM_{2.5}$ mass in Southern Appalachia and the Midwest, regions far removed from major fires.

Relative Roles of Natural and Anthropogenic Emissions. We examined the relative contributions of natural to total emissions using the ratio R_X for each surface grid cell

$$R_X = \frac{C_{B+N}(X)}{C_T(X)}$$

where $C_{B+N}(X)$ denotes the concentration of X from background and natural sources and $C_T(X)$ denotes total concentration of X from all sources. Pollutant X can be ozone, $PM_{2.5}$ mass or the mass of any constituent particulate species. Situations when R_X > 1 indicate a negative response in species X to an increase in emissions (for example, O_3 titration by increased NO emissions). These conditions are more likely to occur during late autumn and winter to ozone when photolysis rates are low although nonlinear nitrate aerosol behavior also occurs. Using ξ^*_{8hO3} to represent C_{O3}, the value of R_{O3} provides a robust

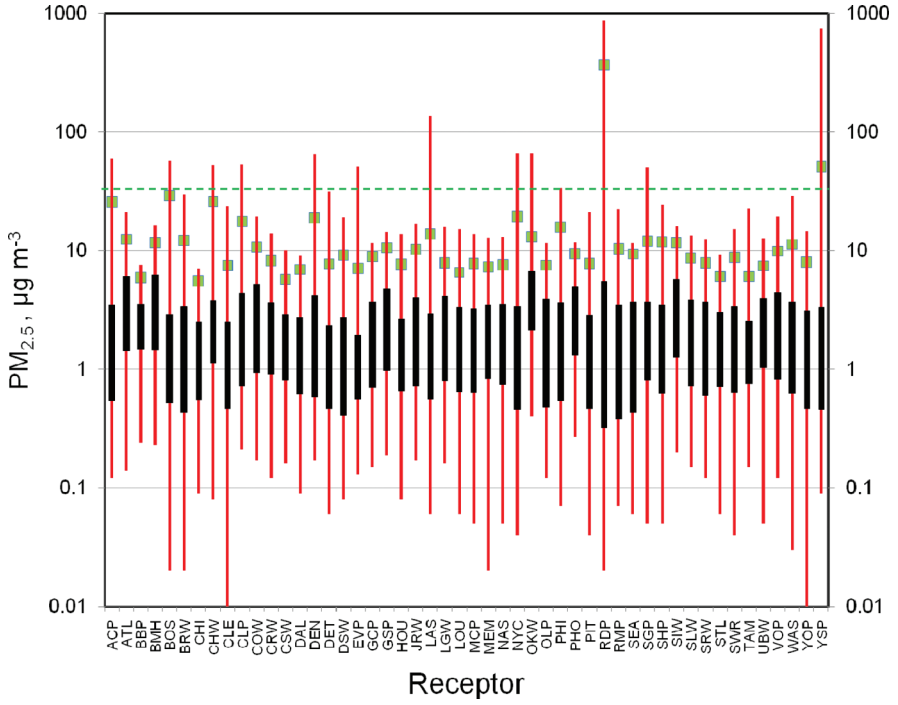

Figure 4. Same as in Figure 2 but for simulated distributions of 24-h average surface $PM_{2.5}$ concentrations at each of 50 receptors based on background plus natural emissions. The 24-h air quality standard of 35 μg m^{-3} is shown by the dashed line. Site locations are shown in Supporting Information, Figure S-3.

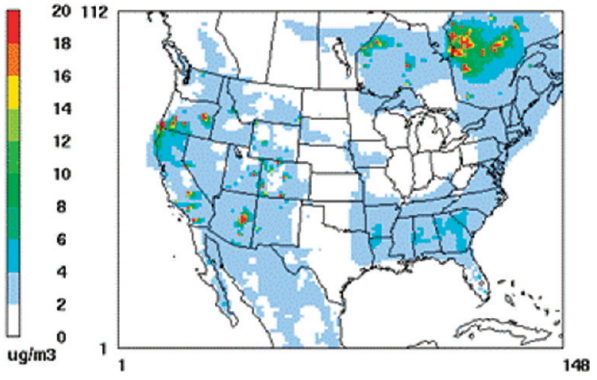

Figure 5. Simulated annual average $PM_{2.5}$ from natural emissions in 2002.

indicator of the role of natural emissions in influencing ozone regulatory compliance.

The April−October ozone season in the U.S. is the primary focus of regulatory efforts. In each of four U.S. regions, R_{O3} varies throughout the ozone season with the highest values toward the beginning (i.e., April) and end (October) and the lowest values occurring in middle to late summer (Supporting Information, Figure S-9). In the west R_{O3} tends to be higher because of wildfires and the lower density of anthropogenic emissions. The Midwest, with the highest density of anthropogenic emissions, experiences the lowest R_{O3}

We computed R_{SO4}, R_{NO3}, R_{OC}, R_{EC}, and $R_{PM2.5}$ using 24-h average concentrations throughout 2002. The annual mean R_{NO3} was >1 nearly everywhere because, in the absence of anthropogenic SO_2 emissions, sulfate aerosol levels are lower and ammonia is freed to combine with nitric acid and make more nitrate aerosol. Generally, R_{SO4}, R_{OC}, R_{EC}, and $R_{PM2.5}$ are much less than R_{NO3} and R_{O3}. As seen in Figure 6, R_{SO4} is <0.2 over most of the U.S., a direct consequence of the many anthropogenic SO_2 sources in that part of the country. B + N sulfate contributions increase across the western U.S. rising above 20% along the Rocky Mountains and reaching to near 60% in areas with wildfires.

The pattern (Figure 6) for R_{EC} indicates that less EC is from natural and background sources than sulfate with R_{EC} < 0.2 except for wildfire-prone areas in the West. However, OC has a very large natural component and R_{OC} < 0.4 only in a narrow band from the central Great Plains northeastward into the upper Midwest. Values for $R_{PM2.5}$ imply that $PM_{2.5}$ is dominated by natural sources across the western third of the continental U.S. with anthropogenic sources dominant to the east.

Table 1 provides mean R_{O3} and $R_{PM2.5}$ values for conditions of special regulatory significance: days when ξ^*_{8hO3} > 75 ppbV and C_{24hPM} > 35 μg m^{-3}. There is no correlation between $R_{PM2.5}$ and $PM_{2.5}$ concentration. In the East, on days with C_{24hPM} > 35 μg m^{-3}, simulated $R_{PM2.5}$ averaged <15% whereas it was nearly 70% in the West. However, R_{O3} varies significantly with ξ^*_{8hO3} and the regression equations relating these variables are provided in Table 1. In addition, R_{O3} > 1 occurs on a significant number of days and both regions have similar ξ^*_{8hO3} thresholds that separate the days when anthropogenic emissions tend to increase or decrease ξ^*_{8hO3}. By counting the days that fall below the ξ^*_{8hO3} threshold it is possible to estimate the frequency of days when ξ^*_{8hO3} will increase from decreases in anthropogenic O_3 precursor emissions.

REGULATORY IMPLICATIONS

While wildfire emissions are included in air quality modeling for regulatory decision-making, lightning NO_x emissions have mostly been ignored. Our work suggests that it is unwise to

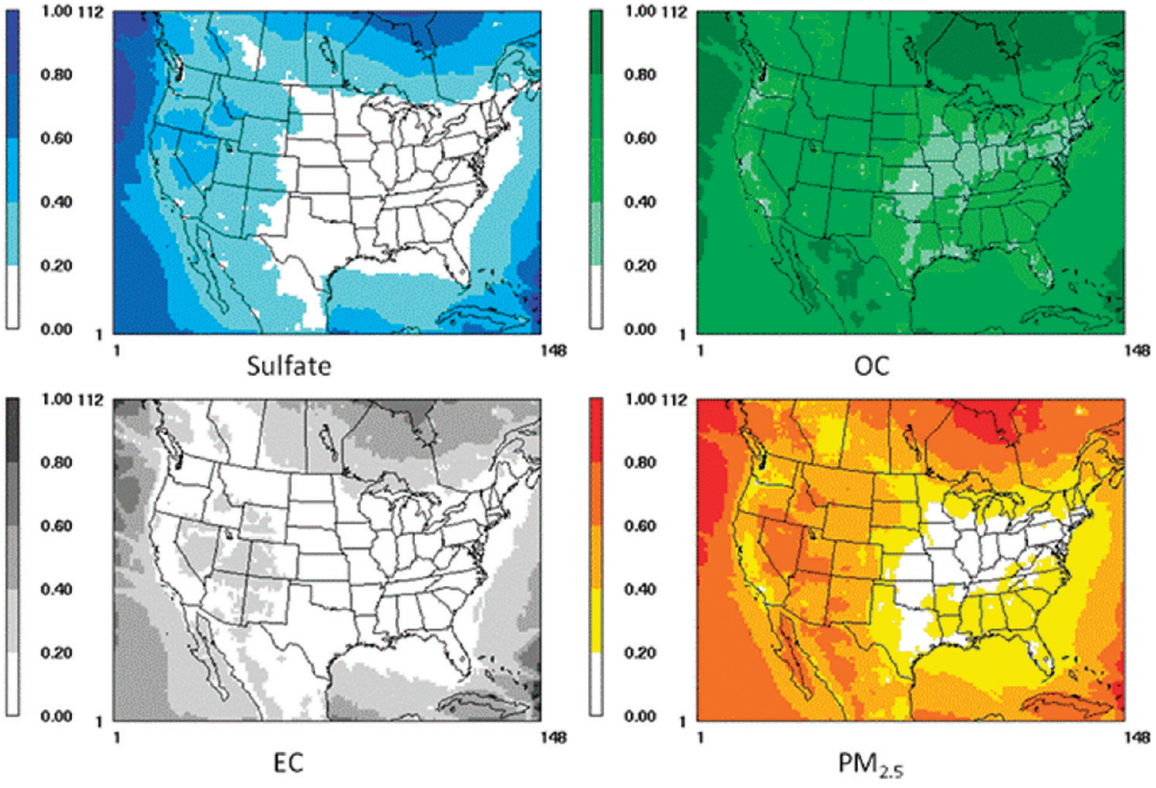

Figure 6. Annual average ratios of B + N to total particle concentrations for sulfate, OC, EC, and $PM_{2.5}$.

Table 1. Natural/Total Concentration Ratios for Pollution Levels of Regulatory Significance

region	ave $R_{PM2.5}$ when $C_{24hPM} > 35\ \mu g\ m^{-3}$	av R_{O3} when $\xi^*_{8hO3} > 75$ ppbV	ξ^*_{8hO3} threshold[a] for $R_{O3} < 1$	$R_{O3} = f(x)$, CD[b] ($x = \xi^*_{8hO3}$)
East	0.14	0.39	30 ppbV	$R_{O3} = 16.02x^{-0.82}$, 0.81
West	0.69	0.61	26 ppbV	$R_{O3} = 3.78x^{-0.41}$, 0.39

[a] Days exceeding threshold are those most likely to experience O_3 increases from increases in anthropogenic emissions, while days below threshold are most likely to experience O_3 increases in response to decreases in anthropogenic emissions. [b] CD = coefficient of determination (i.e., fraction of variance explained by regression). Both regression equations tend to underestimate R_{O3} for days with ξ^*_{8hO3} < threshold, but the bias is largest for the West.

ignore LNO_x emissions, especially across the southern U.S. The EPA should produce guidance on how to best process LNO_x emissions. Another issue of concern is high background levels of ozone associated with pollutants imported from outside the modeling domain. This issue is especially important during the early part of the ozone season. Background levels of particles are less of a regulatory problem, at least in the eastern U.S., but natural sources remain a significant obstacle to realizing compliance with particulate air quality standards and the Regional Haze Rule. Some 45 of 50 sites experienced multiple modeled natural (including background) 24-h $PM_{2.5}$ concentrations >10 $\mu g\ m^{-3}$. Also, areas across the western and southeastern U.S. had modeled annual average B+N $PM_{2.5}$ concentrations $\geq 5\ \mu g\ m^{-3}$ compared to the current 15 $\mu g\ m^{-3}$ standard. Biogenic emissions were the primary source of fine particles in all parts of the country but wildfires also play a large role in the west. More stringent standards will increase the difficulty of achieving compliance, especially for ozone. However, to meet long-term Regional Haze Rule objectives (i.e., natural visibility) regulators must confront the issue of what really constitutes natural particle levels and they must address natural sources that have been traditionally ignored.

■ ASSOCIATED CONTENT

Supporting Information. Additional material as described in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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